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# Advanced oxidation process for the removal of ibuprofen from aqueous solution: A non-catalytic and catalytic ozonation study in a semi-batch reactor

Soudabeh Saeid[a], Pasi Tolvanen[a], Narendra Kumar[a], Kari Eränen[a], Janne Peltonen[c], Markus Peurla[c], Jyri-Pekka Mikkola[a,b], Andreas Franz[a], Tapio Salmi[a,*]

[a] Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500, Åbo/Turku, Finland
[b] Technical Chemistry Department of Chemistry Chemical-Biological Center, Umeå University, SE-90187, Umeå, Sweden
[c] University of Turku, Laboratory of Electron Microscopy, Department of Industrial Physics and Astronomy, FI-20540, Turku, Finland

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ABSTRACT

The Concern on the availability of clean and safe fresh water and the quality of recycled wastewater are important issues, which require a suitable technology to restore the water quality. Pharmaceuticals in waste water are not easily degraded by conventional water treatment technology. Advanced oxidation processes have been applied to eliminate traces of these compounds from aquatic environments. This study was focused on the degradation of ibuprofen (IBU) in aqueous solutions by catalytic and non-catalytic ozonation. Preliminary experiments were conducted to optimize the ozone concentration in water and to investigate other operation parameters. The operation parameters were: temperature, stirring rate, gas flow rate, pH, and use of Spinchem stirrer to reach higher concentrations of dissolved ozone. In general, the initial concentration of IBU was 10 mg/L, and about 93% of IBU was degraded after 4 h of ozonation under optimal conditions. Additional experiments were carried out to investigate the benefit of applying a solid catalyst. H-Beta and Fe-H-Beta type catalysts were immobilized in the Spinchem rotating bed device. The catalytic experiments illustrated a significant improvement in the degradation rate of IBU. The catalysts were characterized by nitrogen adsorption- desorption, scanning electron microscopy, transmission electron microscopy, X-ray powder diffraction and FTIR.

## 1. Introduction

Freshwater resources are continuously influenced by municipal and industrial pollutants. Increasing chemical contamination and disinfection by products have created a large concern during the recent years. Implementation of environmentally clean and safe chemical technologies, processes and materials are necessary for maintaining the water quality and controlling the water pollution [1–3]. Among the huge amount of diverse organic waste products, pharmaceutical compounds remain in surface water and groundwater. The consumption of pharmaceuticals increase worldwide, and they are active at very low concentrations, which becomes a major concern as it cause risks to the human health and environment [4,5]. Common technologies have been used for the pharmaceutical wastewater treatment. Within conventional methods, such as sewer or direct disposal, wastewater is disposed into rivers and seas. Recent studies reveal that an adequate removal of pharmaceutical compounds is not possible through conventional techniques [6,7].

Pharmaceutical compounds which are mostly released by human and animal excretion can enter the water sources. IBU is an efficient pharmaceutical for relieving pain and reducing fever. Because it relieves pain effectively in almost the whole human body, It is used as a reliever for fever symptoms, menstrual cramps, headaches, arthritis, and many other common pains [8]. The molecular structure of IBU is displayed in Fig. 1.

Ibuprofen (IBU) is a member of the propionic acid group in the Non-steroidal anti-inflammatory drugs (NSAID's) class [6]. $EC_{50}$ values are commonly used in environmental toxicology: algae, daphnia and fish as bioassays. According to the OECD guideline, the toxicity values (EC50) of ibuprofen for the species *Scenedesmus abundans* (water green microalgae) and *Daphnia similis* (common water flea) are 1170 μg/L and 97,000 μg/L, respectively [9,10]. IBU has been identified in a broad range of concentrations in landfill leachate, groundwater, and surface waters. A number of rivers in Europe report concentrations of IBU, for

* Corresponding author.
*E-mail address:* tapio.salmi@abo.fi (T. Salmi).

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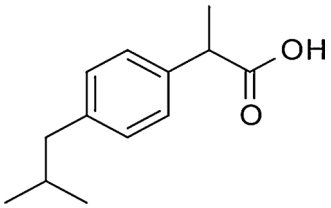


**Fig. 1.** Structural formula of ibuprofen (IBU).

instance in Aura river,Turku, Finland around 20 μg/L, in river Thames, London, UK, around 0.783 μg/L, in smallrivers in UK around 2 μg/L, whereas in river Rakkolanjoki, Finland, a seasonal variation isobserved −0.15 μg/L in February and 0.35 μg/L in May [11–14].

Even low concentrations of IBU can affect the aquatic ecosystem i.e. the accumulation of IBU in food chains can result in a significant influence on the human health and living creatures. For example, the survival of Japanese rice fish (*Oryzias latipes*) can be critical at very low IBU concentrations of 0.0001 mg/L. For this species, IBU can influence on the estrogen homeostasis and thus damage the reproduction [15]. Although IBU has been identified in drinking and surface waters in UK, IBU was found to have 49.5% risk characterization ratio (RCR) in rivers of UK, which according to the study of Boxall et al. is identified as an unacceptable environmental risk [16–18]. It is similarly harmful for the kidney function, an endocrine disruptor, and harms the regeneration in teleostei fish. Also, it may result in hampered embryo movement and hatching in zebrafish [19].

IBU is poorly attenuated by conventional water treatment techniques. Therefore, it is necessary to develop a new and efficient method for removing IBU. A variety of analytical techniques for the determination of IBU such as potentiometric titration, liquid chromatography (LC) [20], supercritical fluid chromatography, spectrophotometry [21], NMR spectrometry and IR spectrometry GC–MS are available [22]. Diverse treatments for eliminating IBU have been proposed, for instance, adsorption on activated carbon, microbial biofilm, biological and physical membrane processes, as well as advanced oxidation processes (AOPs) [23,24]. Among these treatments, AOPs have been widely published in articles devoted to degradation and removal of pharmaceuticals from aqueous environment [25]. In these methods, rapidly reacting, sensitive and non-selective oxidizing species such as hydroxyl radicals are formed, which may oxidize most of the organic matter in water. They are most assuring methods for the removal of pharmaceutical waste products found in water [4]. Furthermore, elimination processes of IBU by AOPs heave been published, for instance by utilizing photo-Fenton, photocatalytic, ultrasound and Fe-based catalysts [26–28]. Ozonation is a widely employed technology for drinking water treatment. These methods are very attractive and, in the vast majority of cases, they transform pollutants into harmless products, including strong oxidizing properties, disinfection potential, and very low selectivity, hence allowing the treatment of a wide range of contaminants. Ozonation has other benefits such as the ability to eliminate a pungent smell. Under the conditions of water treatment, ozone produces hydroxyl radicals. Ozone is an electrophilic molecule and it especially reacts with high electronic density sites of molecules such as organic compounds having carbon–carbon double or triple bonds and aromatics [1,29].

The ozonation process has some confines such as difficulty in eliminating by-products, the low ozone solubility and the stability in water, as well as the selective reactions between ozone and pollutants. Some oxidation processes are slow, while some are incomplete. For this reason, to develop the ozonation process further, it is applied in combination with heterogeneous catalysts to improve the decomposition of ozone and production of hydroxyl radicals [30]. For the removal of organic compounds, such as pharmaceuticals, heterogeneously catalyzed ozonation has been applied [31]. Among heterogeneous catalysts, zeolites have excellent thermal and chemical stabilities in the presence of ozone and therefore they are the more assuring catalysts for long-term ozonation processes [32]. The degradation of IBU by catalysts has been reported in papers such as Fe-based catalytic ozonation with ultrasound and combination of photocatalysis and sonolysis [27,33].

In the present work, non-catalytic and heterogeneously catalyzed ozonation processes have been applied on the degradation of IBU from aqueous solutions. H- and Fe-modified Beta zeolite catalysts were used in a tailored semibatch reactor. In order to optimize the degradation process, five experimental parameters were investigated: temperature, type and position of stirrer, initial concentration of IBU, pH and gas flow rate. The influence of the catalyst amount and the Fe loading on the catalyst were studied.

## 2. Experimental section

### 2.1. Chemicals

IBU ($C_{13}H_{18}O_2$, MW:206.28 g/mol, CAS number:15687-27-1, > 98% purity) was provided in solid state by Sigma Life Science (China). Ethanol ($C_2H_6O$, MW: 46.06 g/mol, CAS number: 64-17-5, > 96% purity) was provided by Altia (Finland). HPLC grade methanol ($H_3COH$, MW:32.04 g/mol, CAS number:67-56-1) provided Vwr Prolabo Chemicals (France) and orto-phosphoric acid 85% ($H_3PO_4$, MW:98 g/mol, CAS:7664-38-2) were used. For the analysis of the concentration of ozone in the aqueous samples, potassium indigo tri-sulfonate ($C_{16}H_7K_3N_2O_{11}S_3$, MW:616.72 g/mol, CAS number:67627-18-3) obtained from Sigma-Aldrich (USA), sodium phosphate monobasic ($H_2$ NaO4P, MW: 119.98 g/mol, CAS number:7558-80-7) provided from Sigma life science (Germany) and orto-phosphoric acid were used and dipropyl-*p*-phenylenediamine (DPD) provided from Merck KGaA (Germany). For the determination of ozone in gas phase, potassium iodide (KI, MW:166 g/mol, CAS number:7681-11-0) was provided from Merck KGaA(Germany), disodium hydrogen phosphate ($Na_2HPO_4$*$2H_2O$, MW:177.99 g/mol, CAS number:10028-24-7) obtained from Sigma-Aldrich (Germany), potassium dihydrogen phosphate ($H_2KO_4P$, MW:136.09 g $mol^{-1}$, CAS number:7778-77-0) was provided from Fluka (Switzerland).

### 2.2. Catalyst preparation

Three different heterogeneous catalysts, H-Beta-25, Fe-H-Beta-EIM-25 and Fe-H-Beta-SSIE-150 were synthesized. The originate zeolites were provided by Zeolyst International. The H-Beta-25 synthesis was done by ion exchange to the form of NH4-Beta-25 by mixing Na-Beta-25 and $NH_4Cl$ at the equimolar ratio in distilled water for 24 h [34]. The H-Beta-25 synthesis was done by the evaporation-impregnation (EIM) method, by stirring the mixture of a ferric nitrate solution and the support for 24 h at 60 °C [35]. The Fe-H-Beta-SSIE-150 was prepared by the solid-state ion exchange method (SSIE) by ball-milling the mixture of the support and iron for 8 h [36]. Later on, these catalysts were dried at 100 °C overnight and calcined at 450 °C for 4 h.

### 2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded with Philips X'Pert Pro MPD using monochromatic CuKα radiation at a voltage of 40 kV and a current of 50 mA. The divergence slit was 0.25° with a fixed 20 mm mask, and the diffractograms were explained with Philips X'Pert highScore MAUD programs. The morphological features of H- and Fe modified zeolite was studied via scanning electron microscopy (SEM) on a Zeiss Leo Gemini 1530 microscope. The specific surface area and pore volume of zeolites were determined by nitrogen adsorption using Carlo Erba Sorptomatic 1900 instrument and calculated by Dubinin method. The catalysts were outgassed at 150 °C for 3 h.

The Fe particle size and structural properties of Fe-H-Beta-25-EIM-Fresh, Fe-H-Beta-25-Regenerated, Fe-H-Beta-150-SSIE-Fresh and Fe-H-